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The Effect of Concentration and Type of Plasticizer on the Mechanical Properties of Cellulose Acetate Butyrate Organic-Inorganic Hybrids

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1. Introduction

Organic/inorganic polymer hybrids is a rapidly growing area of research because they offer opportunities to combine desirable properties of organic polymers (toughness, elasticity, formability) with those of inorganic solids (hardness, chemical resistance, strength). There are several routes to prepare hybrid materials, but one of the most common method is sol-gel technique generating inorganic phase within organic polymer matrix. The advantage of sol–gel technique is mild processing characteristics and the possibility of tailoring morphology of the growing inorganic phase and thus properties of the material by the subtle control of various reaction conditions. This process includes hydrolysis of the precursor (metal alkoxide) followed by condensation reactions of the resulting hydroxyl groups. Considering the nature of the interface between the organic and inorganic phases, hybrid materials can be categorized into two different classes. The first class corresponds to non-covalently bound networks of inorganic and organic phases. These hybrids show weak interactions between the polymer matrix and inorganic phase, such as van der Waals, hydrogen bonding or weak electrostatic interactions and can be prepared by physical mixing of an organic polymer with a metal alkoxide. In the second class organic and inorganic phases are linked through strong chemical bonds (covalent or ionic). Chemical bonding can be achieved by the incorporation of silane coupling groups into organic polymers [1-3].

Cellulose has received a great deal of attention in recent decades as a substitute for petrochemical based polymers. Natural polymer shows however some limitations, for instance with regard to poor processability or high water absorbency. Cellulose esters such as cellulose acetate (CA), cellulose acetate propionate (CAP) and cellulose acetate butyrate (CAB) are less hydrophilic than cellulose, thermoplastic materials [4]. To improve their processability and mechanical properties, the addition of plasticizers is usable. Plasticizers as polymer additives serve to decrease the intermolecular forces between the polymer chains, resulting in a softened and flexible polymeric matrix. They increase the polymer's elongation and enhance processability by lowering the melting and softening points and viscosity of the melts [5].

Plasticizers are often inert organic compounds with low molecular weight, high boiling points and low vapor pressures that are used as polymer additives. The main role of the plasticizer is to improve mechanical properties of the polymers by increasing flexibility, decreasing tensile strength and lowering the second order transition temperature [6]. The International Union of Pure and Applied Chemistry (IUPAC) developed a definition for a plasticizer as a "substance or material incorporated in a material (usually a plastic or an elastomer) to increase its flexibility, workability, or distensibility" [7]. Attributes of a good plasticizer are good compatibility with polymer, which depends on polarity, solubility, structural configuration and molecular weight of plasticizer and results from a similar chemical structure of polymer and plasticizer. Other important factor is plasticizer permanence related to its resistance to migration. Therefore, a good plasticizer should have high boiling point and low volatility (low vapor pressure) to prevent or reduce its loss during processing. Plasticizers should also be aroma free and non-toxic. Another important feature is low rate of migration out of material to preserve desirable properties of plasticized polymer and avoid contamination of the materials from the point of potential health and environmental impacts in contact with it. The permanence of plasticizer in polymer is dependent on the size of the plasticizer molecule, thus the larger molecules, the greater permanence of the plasticizer. The higher diffusion rate of plasticizer in the polymer, the lower permanence due to the migration out of the polymer matrix [8, 9]. Plasticizers influence also processing of the polymers by changing various parameters: viscosity, filler incorporation, dispersion rate, flow, power demand and heat generation [7]. A good plasticizer should also be insensitive to solar UV radiation, stable in a wide temperature range and inexpensive [6]. The efficiency of a plasticizer is defined as the quantity of plasticizer required to provide desired mechanical properties of obtained material [8]. Taking into consideration that effective plasticization is depended on such factors as: chemical structure of the plasticizer, its compatibility and miscibility with the polymer, molecular weight and concentration of plasticizer, rate of diffusion of the plasticizer into the polymer matrix, different polymers require different plasticizers [8].

2. Plasticizer classification

There are two techniques for plasticization: external and internal. External plasticization is a method that provides plasticity through physical mixing. Thus, external plasticizers are not chemically bound to the polymer and can evaporate, migrate or exude from polymer products by liquid extraction [6]. Plasticization of polymers by incorporation of comonomers or reaction with the polymer, providing flexible chain units is called an internal plasticization. Internal plasticizers are groups (flexible segments) constituting a part of a basic polymer chain, which may be incorporated regularly or irregularly between inflexible monomers (hard segments) or grafted as side chains thus reducing intermolecular forces [7, 10-12]. According to the compatibility with the polymer, external plasticizers can be classified into two principal groups: primary and secondary ones, called also extenders. Primary plasticizers have a sufficient level of compatibility with polymer to be able to be used as sole plasticizer in all reasonable proportions, giving a desirable modifying effect. They interact directly with chains. Secondary plasticizers have limited compatibility and will exude from the polymer if used alone. They are used along with the primary plasticizer, as a part of plasticizer system, to meet a secondary performance requirements (cost, low-temperature properties, permanence). Extenders can

be used as lower cost, partial replacement for a primary plasticizer. It is possible that a plasticizer used in one formulation as a primary plasticizer could be used in a second formulation as a second one [10, 11]. Plasticizers, especially used in biopolymer-based films, can also be classified as water soluble and water insoluble. Hydrophilic plasticizers dissolve in polymeric aqueous dispersions and may cause an increase of water diffusion in the polymer when added in high concentration. On the contrary, hydrophobic plasticizers can lead to a decrease in water uptake, due to the closing of micro-voids in the polymer [7].

3. Mechanisms of plasticization

There are several theories that describe the effects of plasticizers and a combination of them allows to explain the concept of polymer plasticization [8, 10, 13-15]:

a. Lubricity theory, developed by Kilpatrick, Clark and Houwink, among others, states that plasticizer acts as a lubricant, reducing intermolecular friction between polymer molecules responsible for rigidity of the polymer. On heating, the plasticizer molecules slip between polymer chains and weaken the polymer-polymer interactions (van der Waals' forces), shielding polymer chains from each other. This prevents the re-formation of a rigid network, resulting in more flexible, softener and distensible polymer matrix.
b. Gel theory, developed by Aiken and others, holds that polymers are formed by an internal three-dimensional network of weak secondary bonding forces (van der Waals' forces, hydrogen bonding) sustained by loose attachments between the polymer molecules along their chains. These bounding forces, are easily overcome by external strain applied to the material, allowing the plasticized polymer to be bend, stretch, or compress. Plasticizer molecules attach along the polymer chains, reducing the number of the polymer-polymer attachments and hindering the forces holding polymer chains together. The plasticizer by its presence separates the polymer chains and increases the space between polymer molecules, thus reducing the rigidity of the gel structure. Moreover, plasticizer molecules that are not attached to polymer tend to aggregate allowing the polymer molecules to move more freely, thus enhancing the gel flexibility.
c. Free volume theory holds that the presence of a plasticizer lowers the glass transition temperature (Tg) of the polymer. Free volume is a measure of internal space available within a polymer matrix. There are three main sources of free volume in polymer: motion of polymer end groups, motion of polymer side groups, and internal polymer motions. When the free volume increases, more space or free volume is provided for molecular or polymer chain movement. A polymer in the glassy state has an internal structure with molecules packed closely and small free volume. This makes the material rigid and hard. When the polymer is heated to above the glass transition temperature, the thermal energy and molecular vibrations create additional free volume which allows greater internal chain rotation and an increase in the segment mobility. This makes the system more flexible and rubbery. When small molecules such as plasticizers are added, the free volume available to polymer chain segments increases and therefore the glass transition temperature lowers.

d. Mechanistic theory of plasticization considers that plasticizer molecules are not bound permanently to the polymer, but rather there is a dynamic exchange process whereby, a constant associations and disassociations of polymer-polymer, polymer-plasticizer and plasticizer-plasticizer molecules form. Some plasticizers form stronger associations with polymer than others. At low plasticizer levels, the plasticizer-polymer interactions are the dominant interactions, what explains "antiplasticization". At high plasticizer loadings plasticizer-plasticizer associations predominate.

Plasticizers have been used as a polymer additives since 1800s [7]. The worldwide plasticizer demand in 2009 was about 5.7 million tons constituting 51.8% share of global polymer additives market [16]. About 100 plasticizers among 1200 different plasticizers produced worldwide are classified as commercially important [7]. Approximately 90% of all plasticizers are used in plasticized or flexible poly(vinyl chloride) (PVC) products [13, 16]. Plasticizers are also required in such polymer systems as poly(vinyl butyral), poly(vinyl acetate), acrylic polymers, poly(vinyldiene chloride), nylon, polyamides, cellulose molding compounds, polyolefins and certain fluoroplastics [7, 17]. The most significant and the largest group of PVC plasticizers is esters of phthalic acid with the share of 97% of all plasticizers used. Phthalate esters plasticizers are mostly based on carboxylic acid esters containing linear or branched aliphatic alcohols of chain lengths C6-C11. Phthalate esters have been used as plasticizers in plastic materials since the 1920s. Widely used phthalates are: di(2-ethylhexyl)phthalate (DEHP), also known as dioctyl phthalate (DOP), di-isononyl phthalate (DINP), di-isodecyl phthalate (DIDP), di-butyl phthalate (DBP) and butyl benzyl phthalate (BBP). The most broadly used since 1930s phthalate plasticizer has been DOP [6, 7]. Phthalate esters are usually added in concentrations up to 50% of the final weight of the products [18, 19]. According to Ceresana Research report, plasticizer market in 2010 was dominated by phthalate esters, with 54% share of DOP, as the most widely used. Ceresana Research forecasts that over the next years DOP will be increasingly replaced by alternative plasticizers due to worldwide growing concerns about the potential toxicity of phthalate esters to humans and the environment [20]. The application of phthalate plasticizers is being questioned because as low molecular weight compounds they migrate out of the polymer matrix. Since they are commonly used in a variety of products: flexible plastics, toys, flooring and car dashboards, food contact materials, packaging systems, synthetic leather, medical devices like blood transfusion bags and haemodialysis tubing, cosmetics, as a result, they have been found in terrestrial and aquatic ecosystems, in domestic foods and wastes, and also in animals and humans. Main human exposure pathways to phthalates include inhalation of air contaminated due to off-gassing from plasticized products, also food and drinking water containing plasticizers that exude from packaging materials designed for victuals or are extracted by the foodstuff [6, 18, 21]. Unfortunately, the exposure to a number of phthalates among the general population is wide, with the highest doses for infants and children, due to additional intake caused by the mouthing behavior of toys. Important exposure pathways of phthalates are food and intensive medical care [6, 22]. There are numerous reports showing that phthalates exert adverse effects on animals' liver, heart, kidney, lungs [23]. A number of studies have been also conducted to evaluate the potential toxicity of phthalate plasticizers on human health. The results showed several implications: hormonal disorders, inducing hepatic

peroxisome proliferation, reproductive toxicity, carcinogenicity, allergic symptoms in children [6, 21, 22, 24, 25]. Public health concerns implied changes in legal provisions. Since 1999, the use of six phthalate plasticizers: DINP, DIDP, DEHP, DBP, BBP and DnOP (di-n-octyl phthalate) in childcare products and toys that can be placed in the mouth of children under the age of three in European Union is restricted. Further regulations in 2005 introduced directive that forbids the use of DEHP, DBP and BBP in any toys and childcare articles within European Union. DEHP, DBP and BBP are also forbidden to be used in cosmetic products and restricted in preparations such as paints and varnishes for end-consumers [18, 22]. The above mentioned reasons caused growing interest in less questioned substitutes of phthalate esters. Commercial used phthalates can be replaced by nontoxic alkyl esters of adipic and citric acids or natural-based plasticizers like epoxidized triglyceride vegetable oils from soybean oil, linseed oil, castor-oil, sunflower oil, and fatty acid esters [7]. The advantages of these alternative additives are good technical performance, processing ease and low toxicity. An important feature of alternative plasticizers is also biodegradability, due to the growing interest of materials obtained from degradable polymers and biopolymers from renewable resources [26, 27]. Other substitutes to phthalates are polymeric plasticizers (for example based on phthalic acid) and oligomers that exhibit low volatility and thus show low rate of migration out of the polymer and leaching tendency. Promising properties show also phenol alkyl sulfonate plasticizers which exhibit excellent gelling capacity thus reducing processing time and temperature. This class of additives shows also reduced leaching tendency and are predestined for medical applications such as polymeric materials exposed to warm, aqueous media for an extended period of time. An interesting, environmentally friendly alternative to phthalates (especially for PVC and poly(methyl methacrylate) are also ionic liquids, however they are still under research [6]. Among esters of bioderived citric acid tributyl citrate, acetyl tributyl citrate, triethyl citrate, acetyl triethyl citrate, and tri(2-ethylhexyl) citrate are of importance. Citric acid esters have been approved as plasticizers for medical plastics, personal care, and according to the U.S. Food and Drug Administration, as additives in food [9, 28]. Citrate esters have been used as effective plasticizers for environmental friendly polymers such as poly(lactic acid), cellulose acetate. However, besides enhanced processability, accelerated degradation rates were also observed [29]. Another class of plasticizers applied in biodegradable polymers are polyols. Among them glycerol, ethylene glycol (EG), propylene glycol (PG), diethylene glycol (DEG), triethylene glycol (TEG), tetraethylene glycol and polyethylene glycol (PEG) are the most often used as polymer additives [6, 7]. Glycerol, which have found application as effective plasticizer for starch or gelatin, and TEG are suitable for use in the food industry as they are on the FDA's Generally Regarded As Safe (GRAS) list [6].

In spite of a wide range of new plasticizers available for polymer industry it must be emphasized that alternative additives may replace traditional ones only in some specific applications due to the several requirements: compatibility, solvation, permanence and price.

There are numerous reports in the literature associated with polymer blends based on cellulose derivatives plasticized with conventional and alternative plasticizers: cellulose acetate plasticized with DEP, triethyl citrate (TEC), and poly(caprolactone triol) (PCL-T), cellulose acetate butyrate plasticized with TEC [27, 30-33].

In our previous work we examined the effect of inorganic phase amount and diethyl phthalate and citrate plasticizer on the degradability of organic-inorganic cellulose acetate butyrate films in sea water [34]. The results of our study showed that the higher the amount of silica incorporated into the CAB with the DEP plasticizer, the higher degradability of the samples. The experiment also showed a synergistic effect of the applied plasticizer on the degradation rate of the CAB/silica hybrids. The CAB/silica hybrids with diethyl phthalate were degraded faster than the hybrids with tributyl citrate due to the higher brittleness of those samples. The aim of the present study is to examine the effects of six different plasticizers: citrate esters and phthalates, on the mechanical properties of cellulose acetate butyrate hybrids.

4. Materials and methods

Cellulose acetate butyrate (CAB, Mn≈ 70000), TEOS (98%) and TEA (99%) were purchased from Sigma-Aldrich. TEC (98%) and TBC (97%) were purchased from Fluka. DEP (99%), DBP (99%) and DOP (99%) were purchased from POCH and used as received. Organic-inorganic hybrids were synthesized according to the procedure we described in patent number 209829 [35]. Cellulose acetate butyrate hybrids were prepared with various amounts of TEOS: 6,25 wt.% and 12,5 wt.%, and various amounts of the chosen plasticizer (25-35%), such as biodegradable citrates: TEC, TEA, TBC and conventional phthalates: DEP, DBP, DOP. Obtained films showed thickness in the range of 0,15-0,18 mm. Samples prepared with concentration below 25% of all investigated plasticizers were too brittle for tensile testing.

Sample compositions and codes are as follows:

a. samples prepared from plasticized CAB: short name of plasticizer (TEC, TEA, TBC, DEP, DBP or DOP)/plasticizer content, e.g. TEC25, DOP35,
b. organic-inorganic hybrids prepared from composition of plasticized CAB and TEOS in 87.5/12.5 polymer/TEOS ratio: amount of TEOS/short name of plasticizer (TEC, TEA, TBC, DEP, DBP or DOP)/plasticizer content, e.g. 12.5TEC25, 12.5DBP30,
c. organic-inorganic hybrids prepared from composition of plasticized CAB and TEOS in 93.75/6.25 polymer/TEOS ratio: amount of TEOS/short name of plasticizer (TEC, TEA, TBC, DEP, DBP or DOP)/plasticizer content, e.g. 6.25TEC25, 6.25DBP30.

A typical preparation of organic-inorganic hybrid was as follows [36]: polymer was placed in a polyethylene beaker and dissolved in acetone. Plasticizer and TEOS was then added and mixed vigorously. To this solution catalytic amount of HCl (0.1 M) was added to initiate the sol-gel process and mixed until it appeared clear and homogenous. The solution was cast in an evaporating PTFE dish and left exposed to atmospheric conditions followed by drying in a vacuum drier at 40^{o}C for 12 hours to ensure complete solvent evaporation.

Mechanical properties were investigated using a universal tensile machine (Instron 5565) at a crosshead speed of 100 mm/min at room temperature (according to the test method described in International Standards PN-EN ISO 527-1:1998, PN-EN ISO-3:1998). Sample dimensions: length 150 mm, width 10 mm. At least five tests were performed for each type of the sample, to ensure the reliability of the test results, and the average was used.

The properties of the materials used in this study are showed in Table 1.

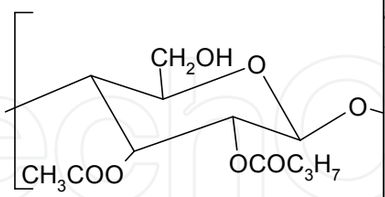
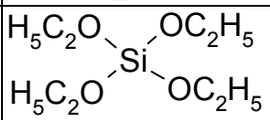
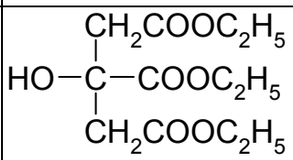
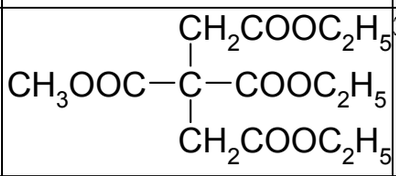
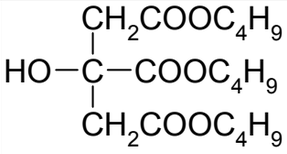
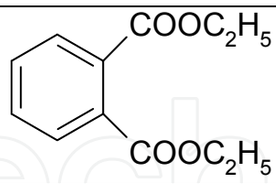
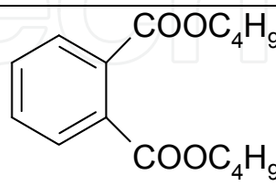
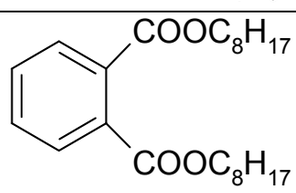
Full name	Short name	Chemical structure	Molecular weight	Vapor pressure	Boiling point
Cellulose acetate butyrate	CAB		average M_n ~70,000	-	- (melting range 150-160°C)
Tetraethoxysilane	TEOS		208.33	<1 mmHg (20°C)	168°C
Triethyl citrate	TEC		276.28	1 mmHg (107°C)	235°C/ 150 mmHg
Acetyl triethyl citrate	TEA		318.32	not available	228-229°C/ 100 mmHg
Tributyl citrate	TBC		360.44	not available	234°C / 17 mmHg
Diethyl phthalate	DEP		222.24	1 mmHg (100°C)	298-299°C
Dibutyl phthalate	DBP		278.34	1 mmHg (147°C)	340°C
Dioctyl phthalate	DOP		390.56	1.2 mmHg (93°C)	384°C

Table 1. Properties of the materials used in this study.

5. Results and discussion

Comparison of mechanical properties of organic-inorganic hybrids and cellulose acetate butyrate with different plasticizers is shown in Table 2 and Figures 1-18.

Type of the plasticizer	Polymer/TEOS ratio					
	87.5/12.5		93.75/6.25		100	
	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)	Tensile strength (MPa)	Elongation at break (%)
TEA 25	24.9 ± 0.5	7.0 ± 0.4	23.0 ±1.3	16.2 ± 1.1	20.1 ± 1.5	26.3 ± 3.0
TEA 30	24.9 ± 1.1	37.8 ± 8.5	23.1 ± 1.3	44.8 ± 9.1	21.6 ± 1.0	34.3 ± 6.1
TEA 35	21.2 ± 1.4	45.6 ± 5.4	21.8 ± 0.8	53.6 ± 4.1	20.4 ± 0.7	48.7 ± 1.1
TBC 25	17.4 ± 0.7	16.7 ± 4.1	16.4 ± 0.4	13.9 ± 1.4	15.5 ± 1.7	24.3 ± 2.3
TBC 30	25.3 ± 2.8	40.9±13.6	23.6 ± 2.5	42.4 ± 7.6	21.8 ± 2.3	30.2 ± 6.9
TBC 35	15.7 ± 1.5	53.1 ± 8.4	14.3 ± 0.8	53.9 ± 2.1	13.4 ± 1.0	38.1 ± 4.4
TEC 25	24.0 ± 0.8	5.0 ± 0.6	17.0 ± 1.6	7.6 ± 1.1	21.5 ± 0.8	14.7 ± 2.4
TEC 30	14.4 ± 0.1	25.8 ± 1.6	13.3 ± 0.4	21.6 ± 3.5	12.7 ± 0.5	29.0 ± 6.3
TEC 35	12.8 ± 0.3	29.3 ± 4.2	11.5 ± 0.3	25.8 ± 0.8	11.2 ± 0.4	32.0 ± 3.8
DEP 25	15.9 ± 0.5	5.5 ± 0.9	13.8 ± 1.7	5.5 ± 0.3	12.5 ± 1.5	8.7 ± 1.7
DEP 30	20.9 ± 0.8	16.3 ± 1.5	19.2 ± 1.1	14.0 ± 2.0	17.6 ± 1.0	10.6 ± 1.7
DEP 35	21.7 ± 1.1	19.9 ± 0.4	17.4 ± 0.9	15.0 ± 3.0	14.1 ± 0.9	17.8 ± 0.6
DBP 25	23.2 ± 1.7	19.3 ± 3.5	20.5 ± 1.6	23.6 ± 2.8	21.0 ± 1.7	25.5 ± 2.5
DBP 30	26.4 ± 0.8	33.9 ± 5.0	25.0 ± 0.6	35.6 ± 4.6	24.8 ± 0.3	31.8 ± 5.5
DBP 35	20.3 ± 0.7	48.6 ± 5.6	16.4 ± 0.5	36.1 ± 3.1	14.6 ± 0.2	37.2 ± 2.8
DOP 25	27.3 ± 2.8	28.7 ± 0.4	23.7 ± 1.6	21.4 ± 1.7	22.3 ± 1.6	13.8 ± 2.8
DOP 30	31.1 ± 1.2	52.1 ± 1.5	28.1 ± 2.5	42.5 ± 4.5	28.3 ± 1.8	34.3 ± 2.0
DOP 35	23.5 ± 3.9	50.1 ± 3.3	19.9 ± 2.1	40.4 ± 6.1	16.7 ± 1.1	38.0 ± 5.0

Table 2. Mechanical properties of CAB samples containing various plasticizers.

The aim of adding plasticizer to CAB-hybrids is to reduce natural brittleness of the polymer and to enhance plastic elongation, while providing optimal tensile strength and stiffness.

The plasticizing efficiency of the investigated phthalates and citrates evaluated by tensile testing is summarized in Table 2. At concentration 25% samples of the cellulose acetate butyrate plasticized with TEA, TEC, DBP and DOP exhibited similar tensile strength in the range of 20 – 22 MPa, however high values of elongation at break (24 – 26%) showed only samples containing TBC, DBP and TEA. In case of CAB hybrids the introduction of inorganic phase into polymer matrix caused hardening and reinforcing of the material, thus an increase of tensile strength in comparison with unmodified CAB was observed. Regarding organic-inorganic hybrids prepared from 93.75/6.25 and 87.5/12.5 polymer/TEOS formulations the highest values of tensile strength (23 – 24 MPa and 25 – 27 MPa) were obtained for samples 6.25TEA25, 6.25DOP25, and 12.5TEA25, 12.5DOP25, respectively. However, at the same time, obtained samples exhibited lower values of elongation at break as compared with plasticized CAB, due to the higher brittleness of the material. The results showed that the presence of 25% of plasticizer in organic-inorganic CAB hybrids was insufficient for providing acceptable flexibility.

Considering the effect of plasticizer concentration it can be concluded that all of the plasticizers investigated, excluding TEC, caused an antiplasticization at concentration 30% of the plasticizer, resulting in an increase in tensile strength in comparison with the values at 25%. To the contrary, samples plasticized with TEC showed a common trend: with increasing plasticizer content, the tensile strength decreased, while elongation at break increased. Antiplasticizing effects were previously observed by Donempudi et al. for PVC membranes plasticized with phthalates [37], reported for citrate esters used as plasticizers for poly(methyl methacrylate) (PMMA) [38], and also has been found for polycarbonate, polysulfone, polystyrene plasticized with various plasticizers [39]. Even though the phenomenon of antiplasticization has been already long observed in synthetic polymers, the mechanisms involved are not perfectly known. According to Anderson et al. the phenomenon can be attributed to a chain end effect. Antiplasticizers initially fill unoccupied lower volume at the chain end and then the overall polymer free volume. Chain end mobility is restricted, resulting, thus, in higher modulus and resistance, generally followed by polymer hardness. Jackson and Caldwell suggested that antiplasticization can be attributed to a free volume reduction due to antiplasticizers [40]. Another explanation is an increase in the degree of order or the crystallinity of the system, resulting in an increase in tensile strength. Antiplasticization of the samples may be attributed to the hindered local mobility of the macromolecules, and thus reduced flexibility, due to the strong interaction between polymer and plasticizer (i.e. hydrogen bonding, van der Waals' forces) [39, 41]. Antiplasticization in polymers depends on molecular weight and concentration of the diluent and occurs over a concentration range below the plasticization threshold. This point, dividing antiplasticization and plasticization behavior, is typical for each polymer–plasticizer system [42]. Gutierrez-Villarreal [38] reported an antiplasticization effect for PMMA plasticized with TEC at low concentration of plasticizer (about 13 wt%). The plasticization threshold for TEC plasticized samples based on CAB was not observed in the range of concentrations used in this study. For the samples prepared with lower concentration of TEC (below 25%) the measurement using a universal tensile machine was

difficult to perform due to the high brittleness of the organic-inorganic hybrids (cutting of the samples might induce micro-cracking on the edge of the samples and influence the reliability of the test results).

Considering the fact that different factors may be involved in the antiplasticization phenomenon, the present study was not designed to provide evidence in support of any one of these mechanisms. Further experiments including dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) or X-ray measurements could confirm suggested hypothesis.

At concentration 30% the CAB samples plasticized with DOP and DBP showed the highest tensile strength (28.3 MPa and 24.8 MPa, respectively). Among citrate plasticizers the higher tensile strength values were obtained for CAB samples plasticized with TBC and TEA (21.8 MPa and 21.6 MPa, respectively). The lowest values of tensile strength showed CAB samples plasticized with TEC (12.7 MPa) and DEP (17.6 MPa) due the high brittleness of the material, indicating low plasticizing efficiency of those plasticizers. Interestingly, organic-inorganic hybrids showed both high values of tensile strength, regardless of the plasticizer type and concentration, as well as elongation at break in comparison with plasticized CAB. Organic-inorganic hybrid prepared from 87.5/12.5 polymer/TEOS formulation and DOP (12.5DOP30) exhibited the highest tensile strength (31.1 MPa) as well as very high elongation at break (52.1%). Regarding the citrate plasticizers at 30% concentration the best mechanical properties were obtained for TBC and TEA. In this case, organic-inorganic hybrids prepared from 87.5/12.5 polymer/TEOS formulation plasticized with TBC and TEA showed similar values of tensile strength and elongation at break: 25.3 MPa and 40.9%, and 24.9 MPa and 37.8% , respectively.

At higher concentration of plasticizers used in this study (35%) the additives caused plasticization reflected as a decreases in tensile strength and an increase in elongation at break values. Regarding CAB samples, the highest values of elongation at break showed material plasticized with TEA (48.7%). Among phthalates, at level of 35%, the highest value of elongation at break CAB reaches for DOP and DBP (38.4% and 37.2%, respectively). The highest values of elongation at break for the organic-inorganic hybrids obtained from 93.75/6.25 polymer/TEOS formulation were observed for samples plasticized with TBC, TEA and DOP (53.9%, 53.6% and 40.4%, respectively). In case of organic-inorganic hybrids obtained from 87.5/12.5 polymer/TEOS formulation the highest values of elongation at break provided TBC, DOP and DBP plasticizers (53.1%, 50.1% and 48.6%, respectively).

If one considers the effect of plasticizer molecular weight on the mechanical properties of investigated samples, one might conclude that the higher molecular weight, the better efficiency of the plasticizer. Regarding phthalate esters, plasticizer with the lowest molecular weight produced the less flexible samples and the efficiency varied in the order DEP>DBP>DOP. Similar behavior was previously observed for phthalate esters used as plasticizers for PVC membranes [37]. Donempudi at al. found that the tensile strength of the membranes decreased as the size of the alkyl group of the phthalate molecule increased from methyl to octyl, meanwhile the elongation at break values increased. They referred that an increase in the size of the alkyl chain length of the phthalate molecule brought about

an increased dilution of the polymer solution. Hence, the high molecular weight implied a further reduction in the number of macromolecules per unit volume. Therefore, the use of higher concentration of larger size phthalate molecules in the PVC matrix caused significant dilution effect, and as a result an increase in the flexibility of the polymer [37]. Similar results were obtained also for citrate plasticizers applied in the study. The lowest plasticizing efficiency of TEC, among citrate plasticizers used in this work, may be attributed to its low molecular weight. On the contrary, the highest molecular weight TBC, containing longer alkyl groups was found to be the most efficient.

The stress-strain curves for the samples prepared with different plasticizers are presented in Fig. 1-18. The characteristic type of the curve for hard and rigid materials, exhibiting low values of elongation at break, showed organic-inorganic hybrids prepared with 25% of TEC and DEP (Figure 7, 10). Hard, tough behaviour is observed for the samples exhibiting sufficient and good plasticizing efficiency (Fig. 1-6, 8, 9, 11-18). All the curves showed cold drawing and strain hardening in the final section of the curve. However, for the samples prepared from the formulations exhibiting the best mechanical properties, the curves showed better defined yielding point. In case of organic-inorganic hybrids with the highest content of inorganic phase the curves exhibited elastic deformation in smaller strain ranges than for the plasticized CAB.

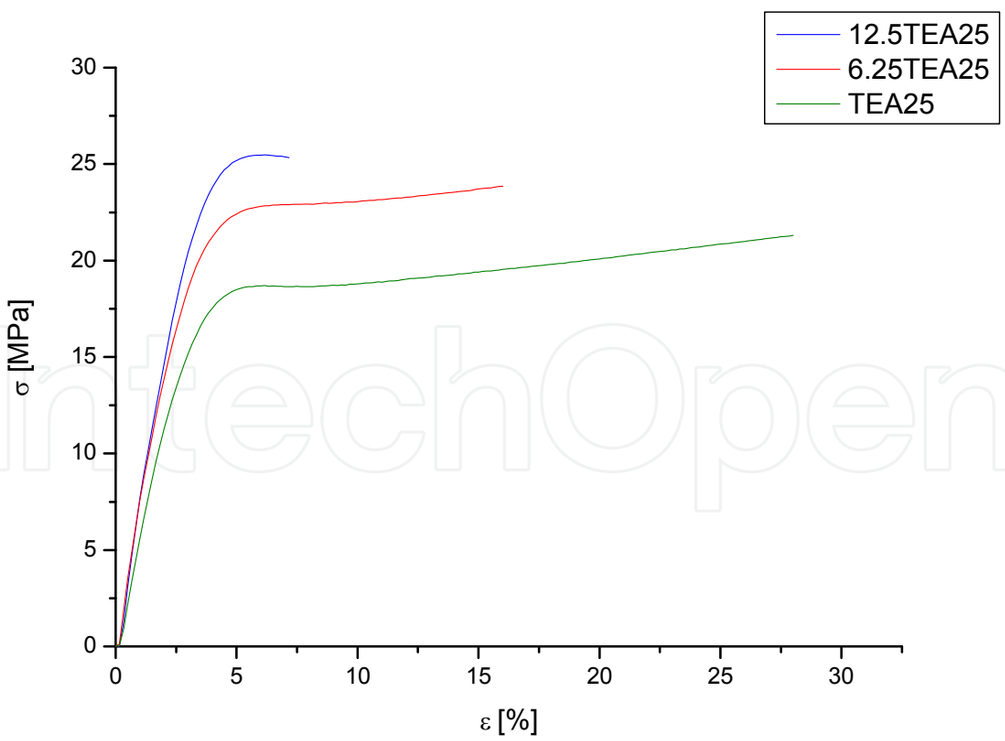


Fig. 1. The tensile stress-strain curves for samples prepared with 25% of TEA.

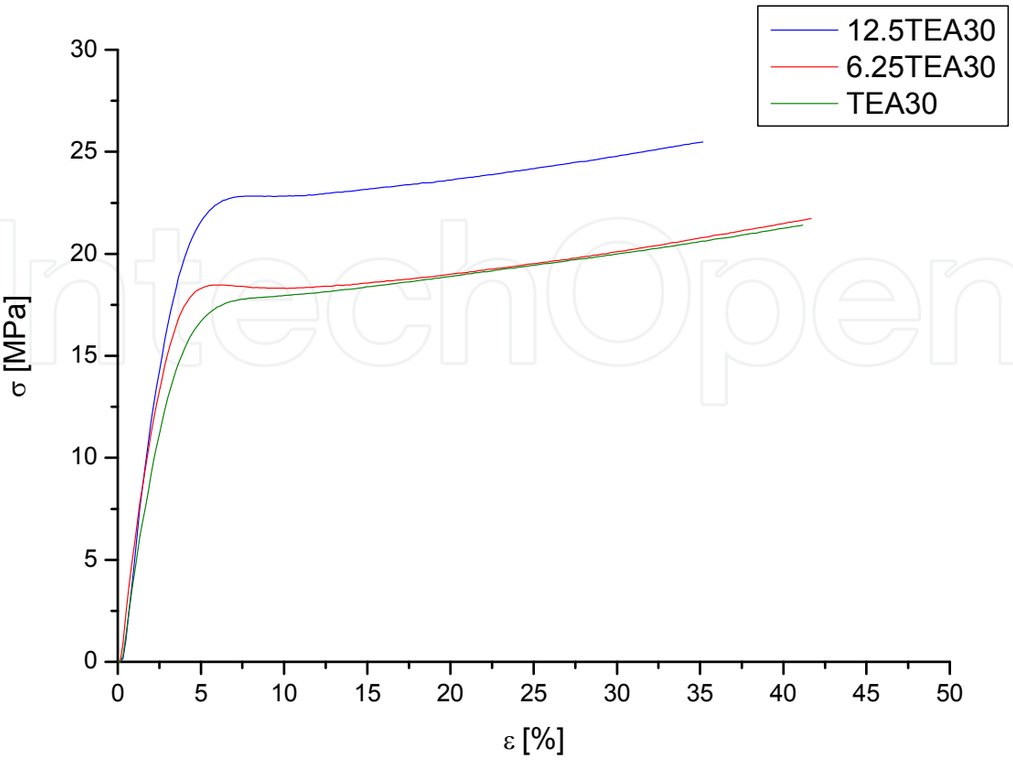


Fig. 2. The tensile stress-strain curves for samples prepared with 30% of TEA.

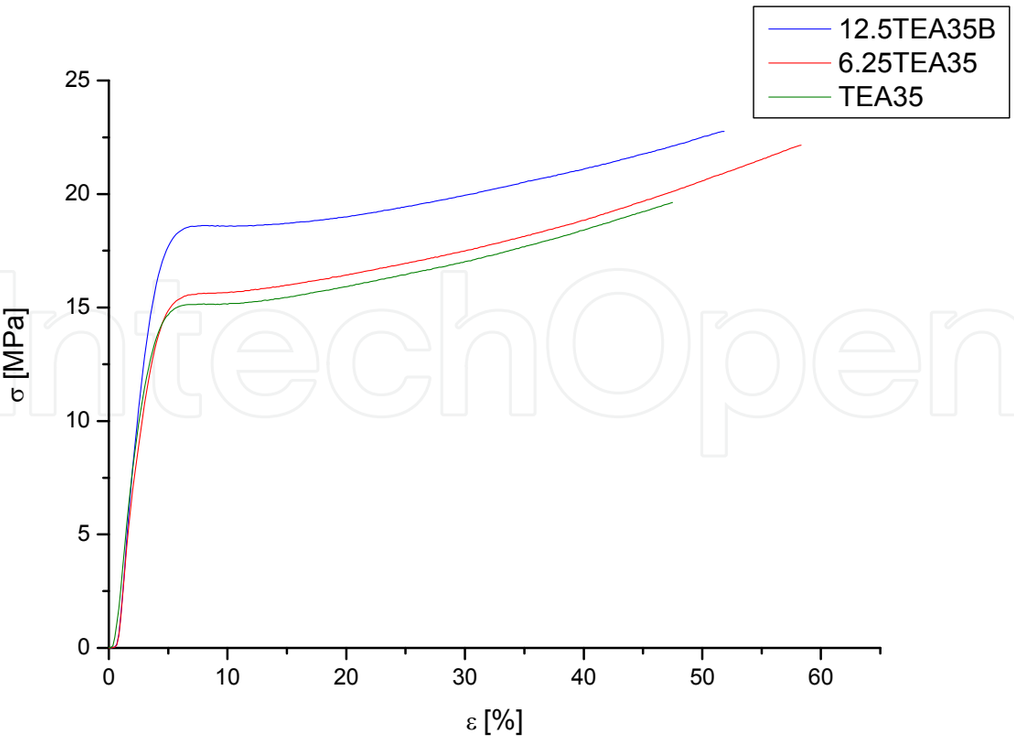


Fig. 3. The tensile stress-strain curves for samples prepared with 35% of TEA.

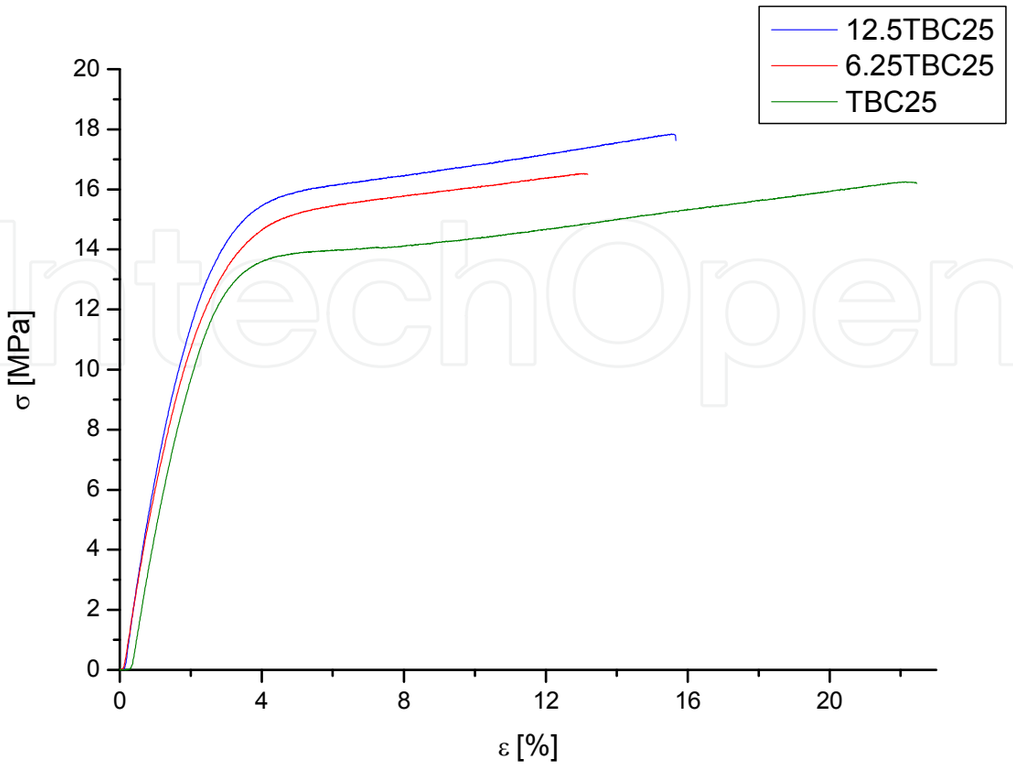


Fig. 4. The tensile stress-strain curves for samples prepared with 25% of TBC.

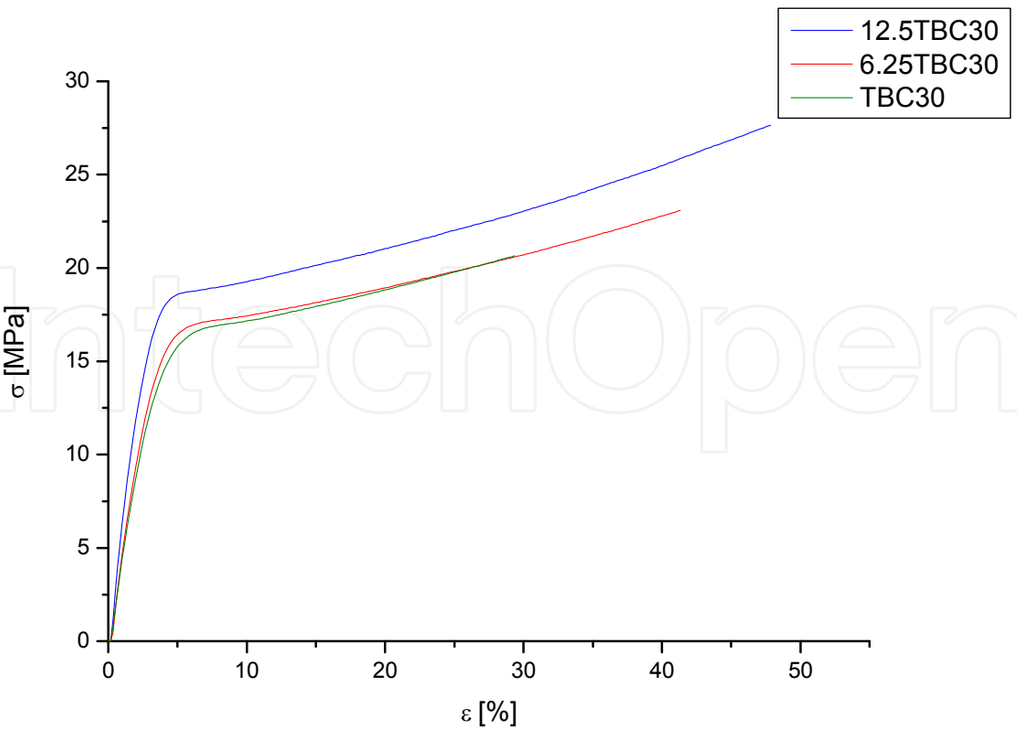


Fig. 5. The tensile stress-strain curves for samples prepared with 30% of TBC.

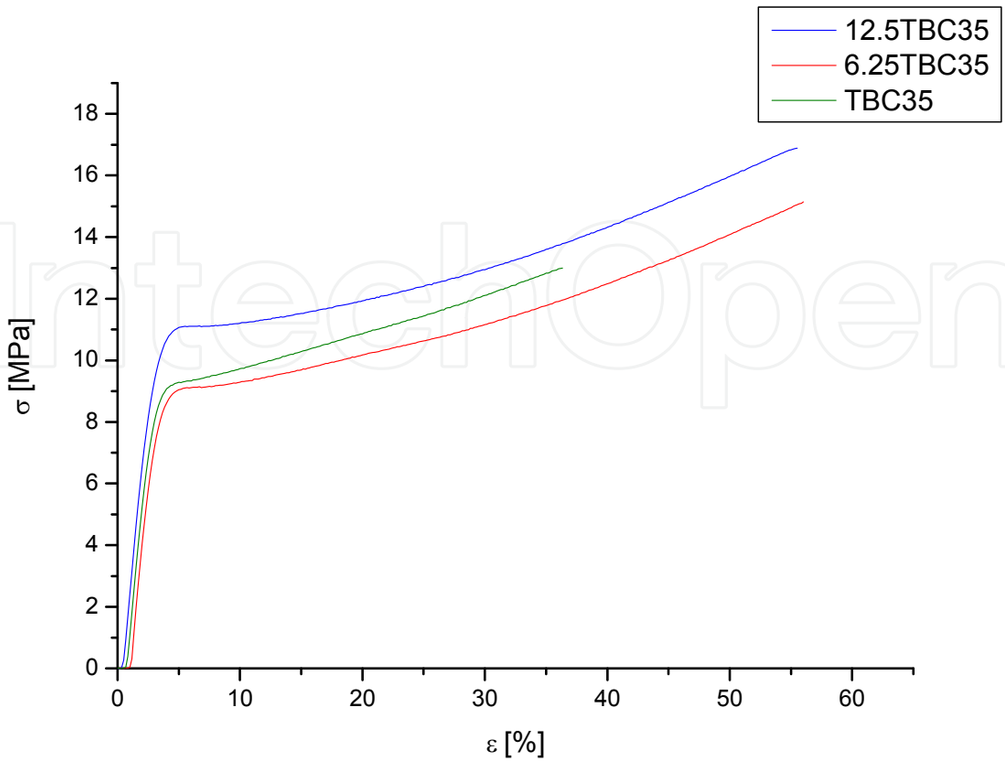


Fig. 6. The tensile stress-strain curves for samples prepared with 35% of TBC.

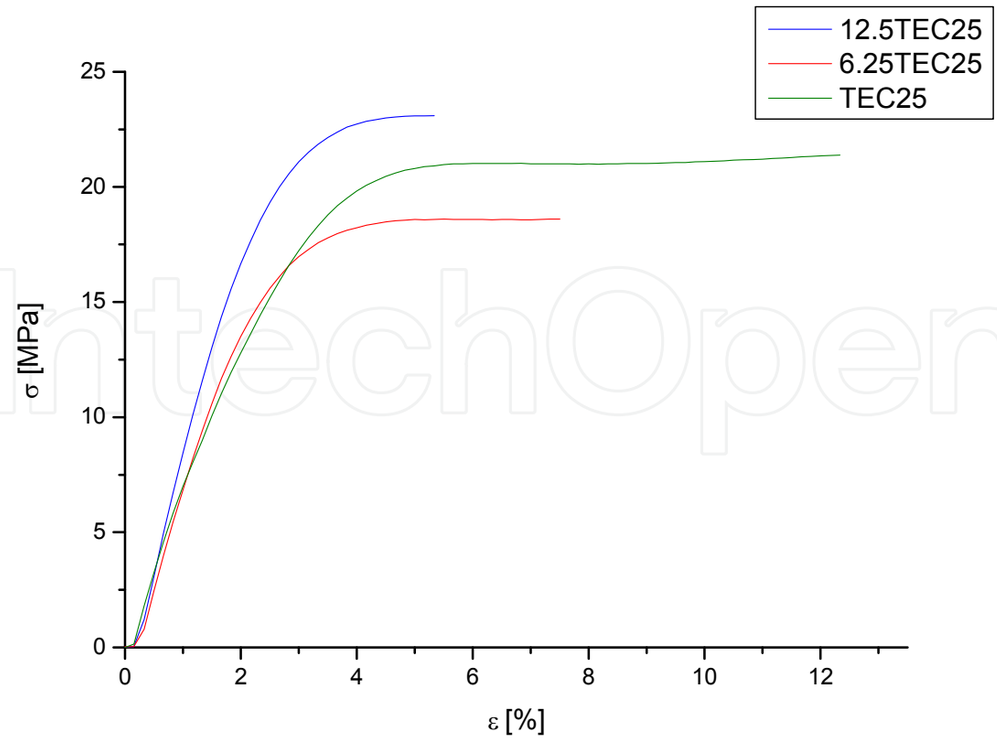


Fig. 7. The tensile stress-strain curves for samples prepared with 25% of TEC.

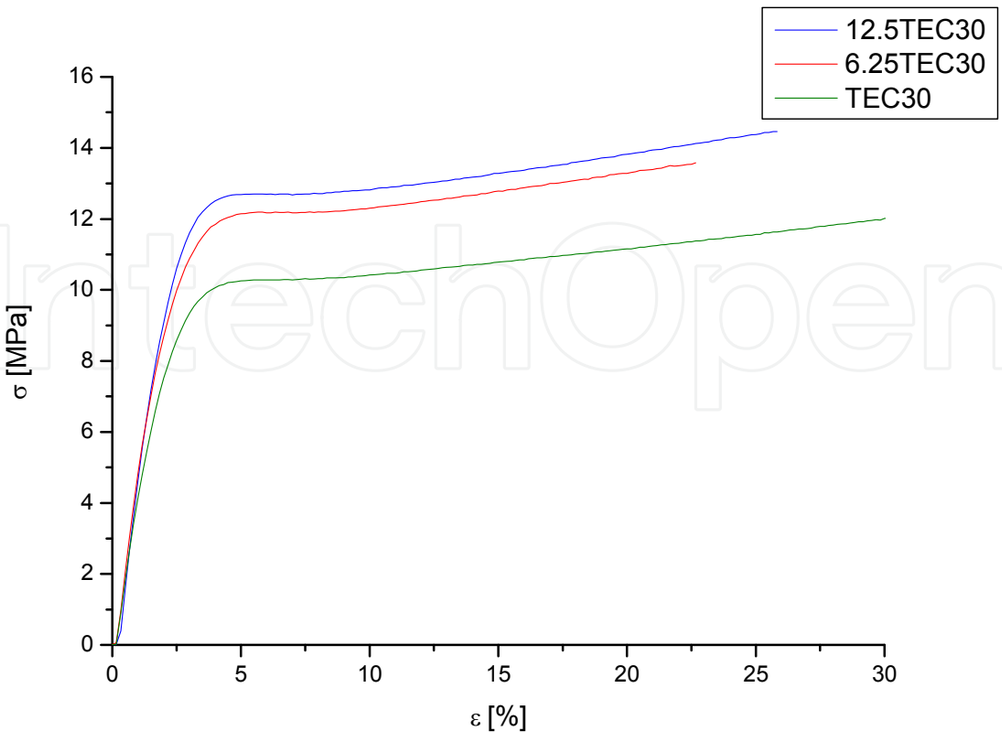


Fig. 8. The tensile stress-strain curves for samples prepared with 30% of TEC.

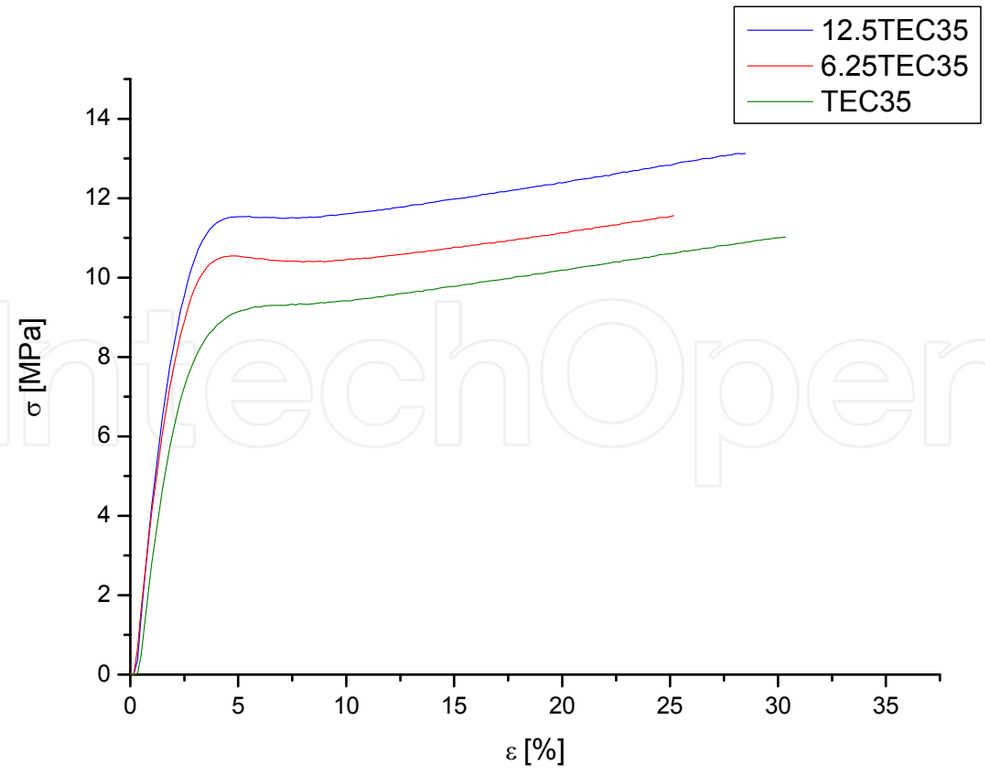


Fig. 9. The tensile stress-strain curves for samples prepared with 35% of TEC.

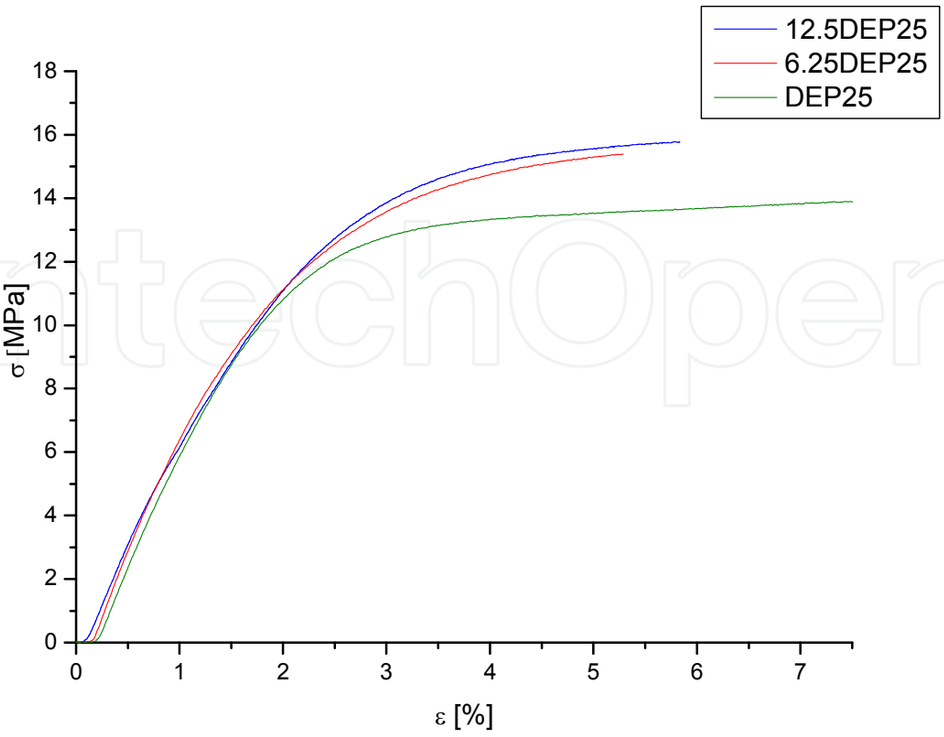


Fig. 10. The tensile stress-strain curves for samples prepared with 25% of DEP.

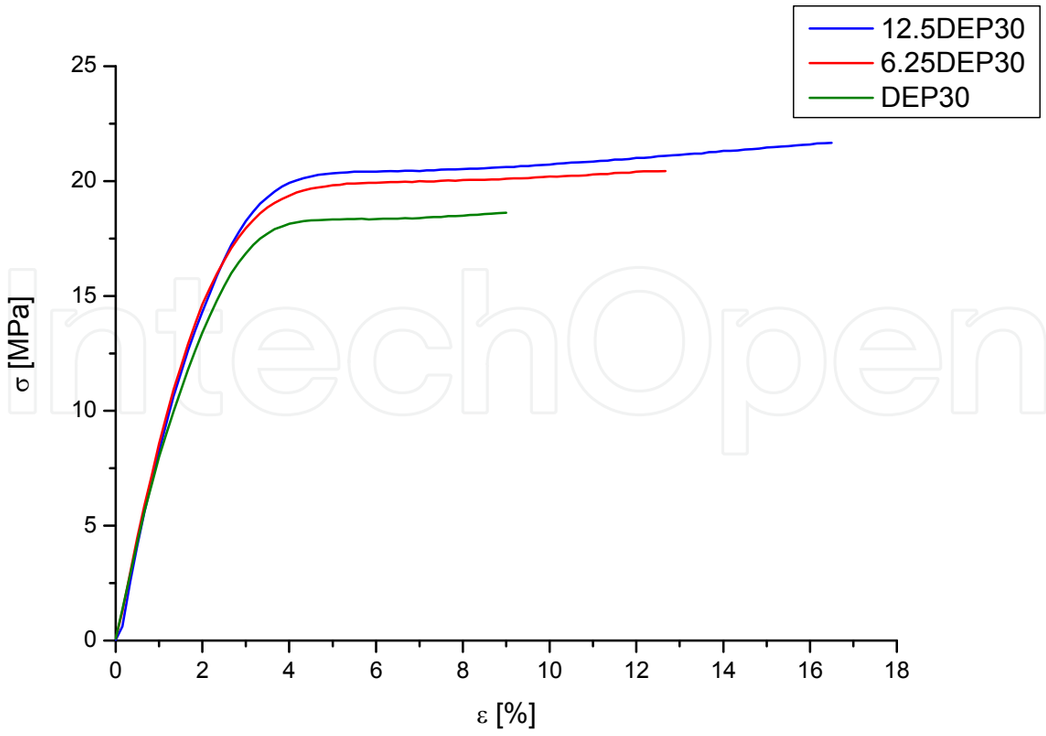


Fig. 11. The tensile stress-strain curves for samples prepared with 30% of DEP.

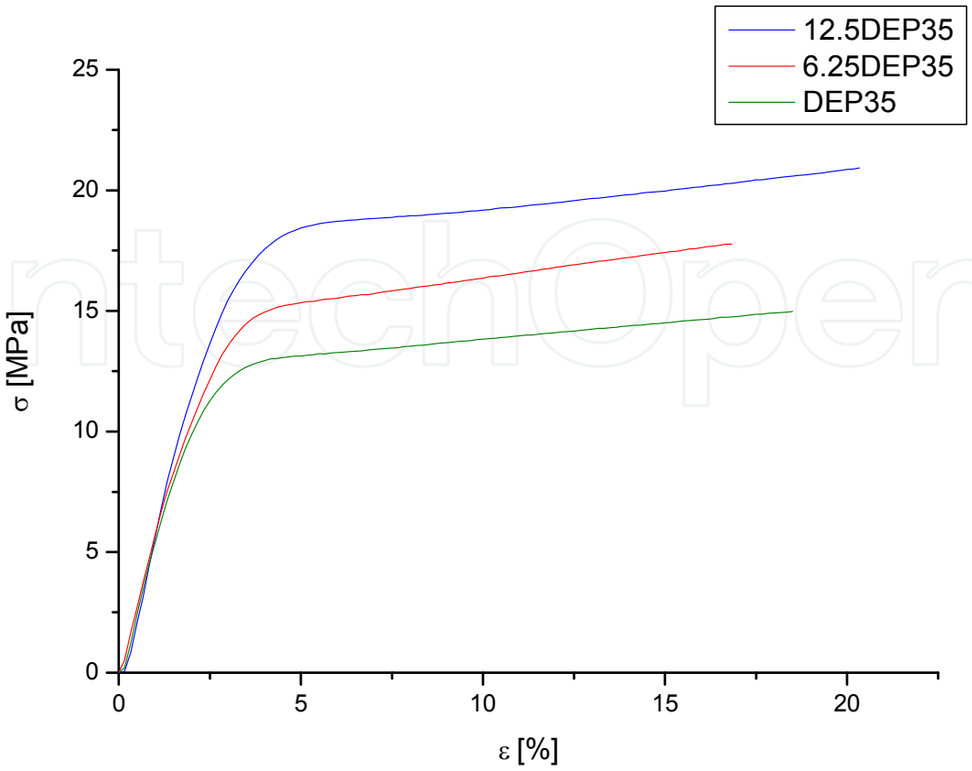


Fig. 12. The tensile stress-strain curves for samples prepared with 35% of DEP.

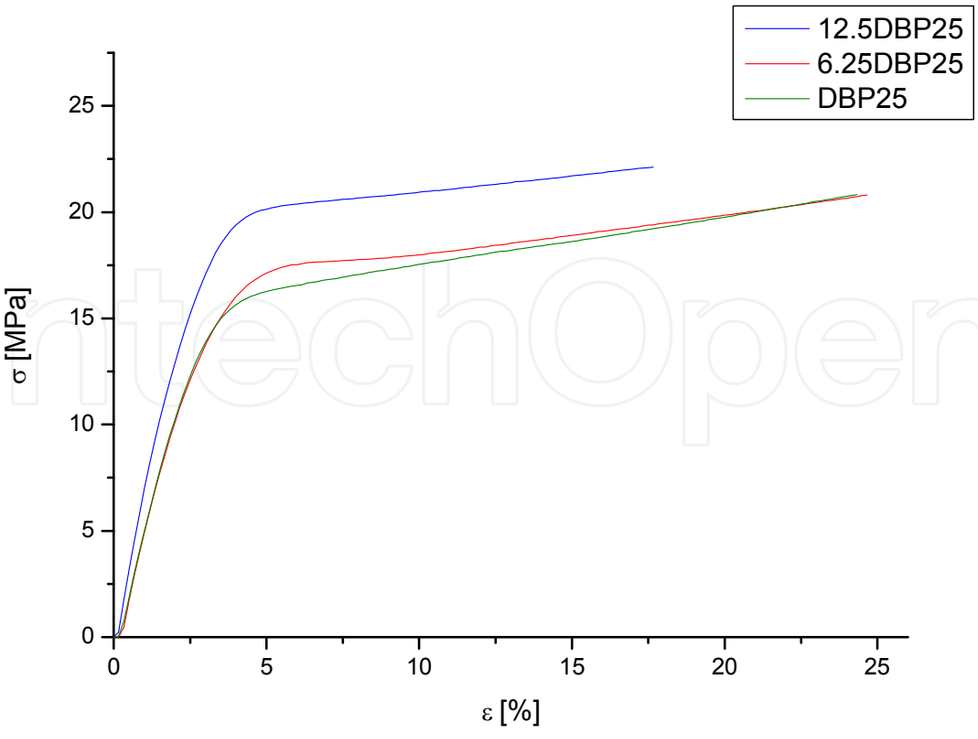


Fig. 13. The tensile stress-strain curves for samples prepared with 25% of DBP.

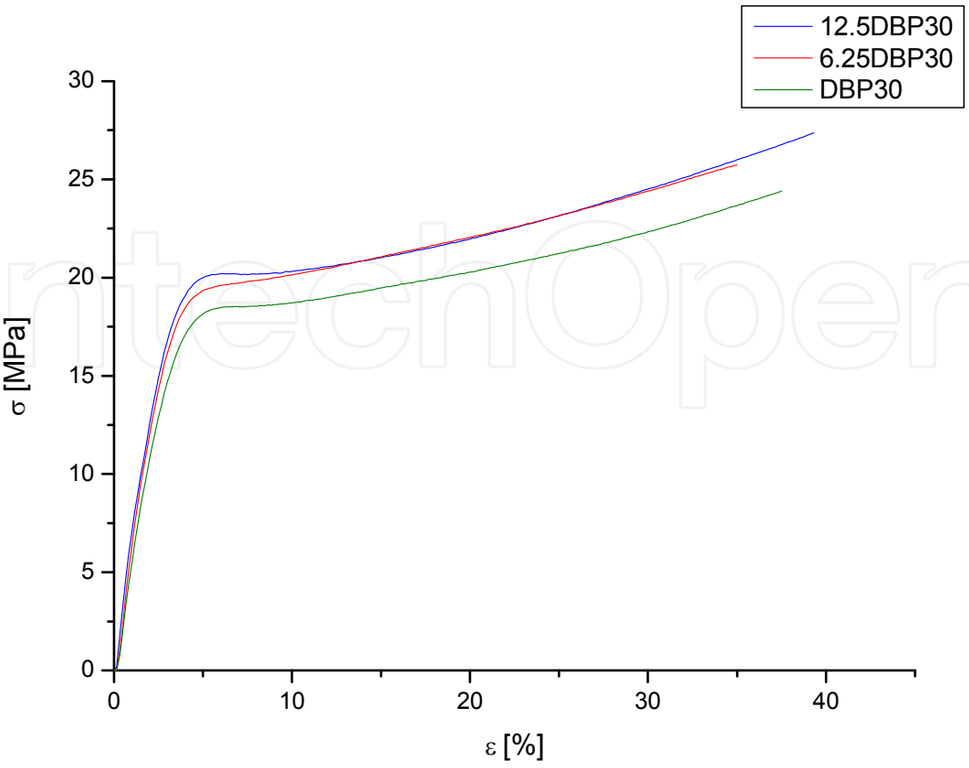


Fig. 14. The tensile stress-strain curves for samples prepared with 30% of DBP.

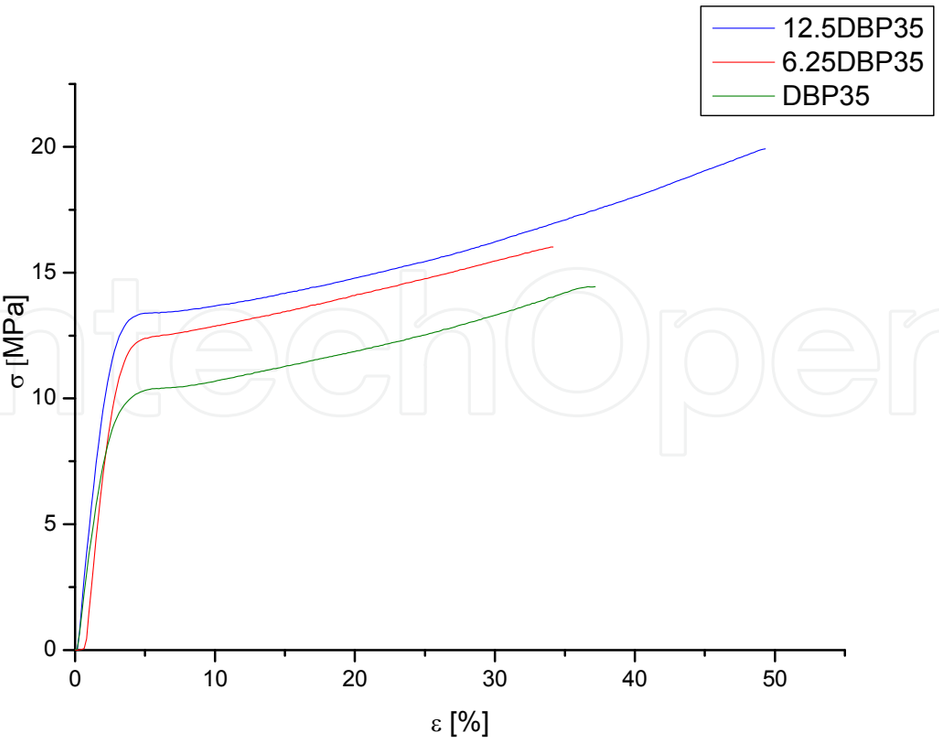


Fig. 15. The tensile stress-strain curves for samples prepared with 35% of DBP.

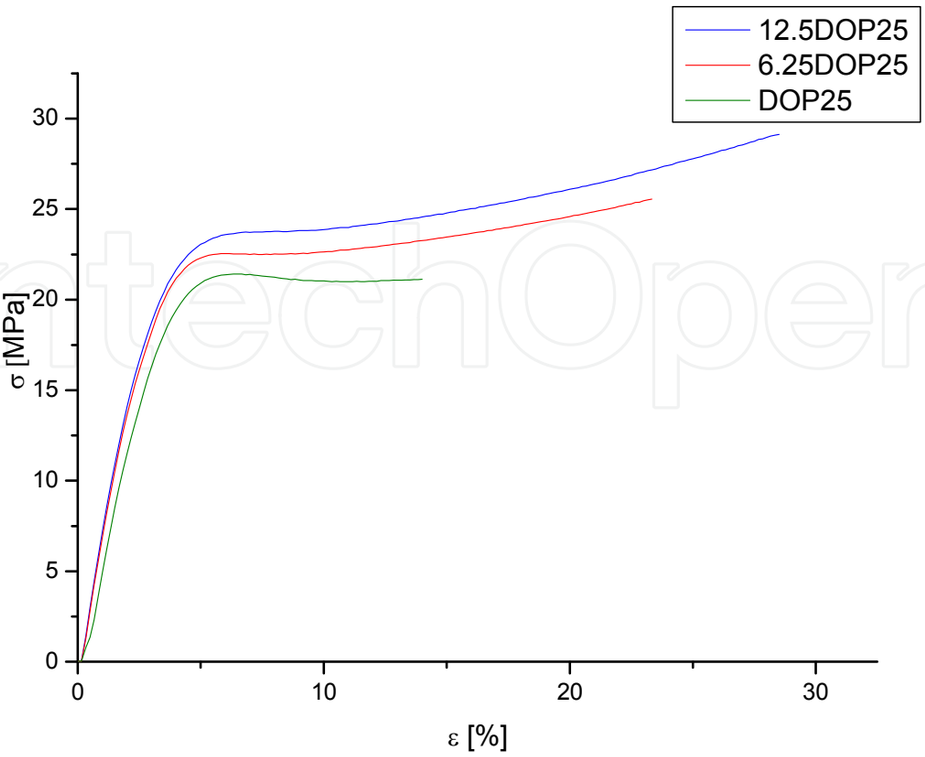


Fig. 16. The tensile stress-strain curves for samples prepared with 25% of DOP.

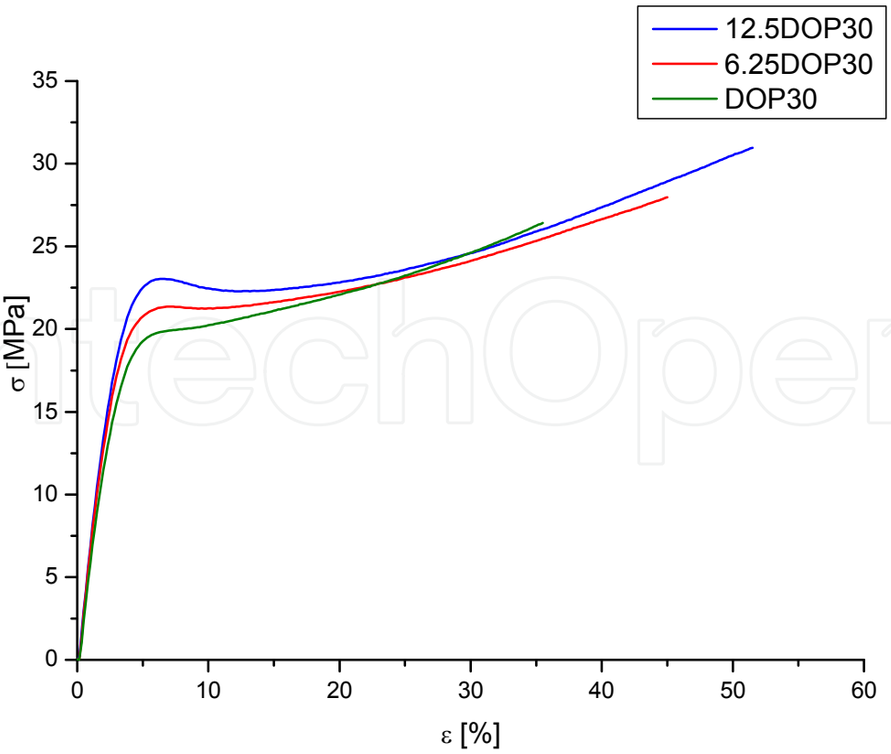


Fig. 17. The tensile stress-strain curves for samples prepared with 30% of DOP.

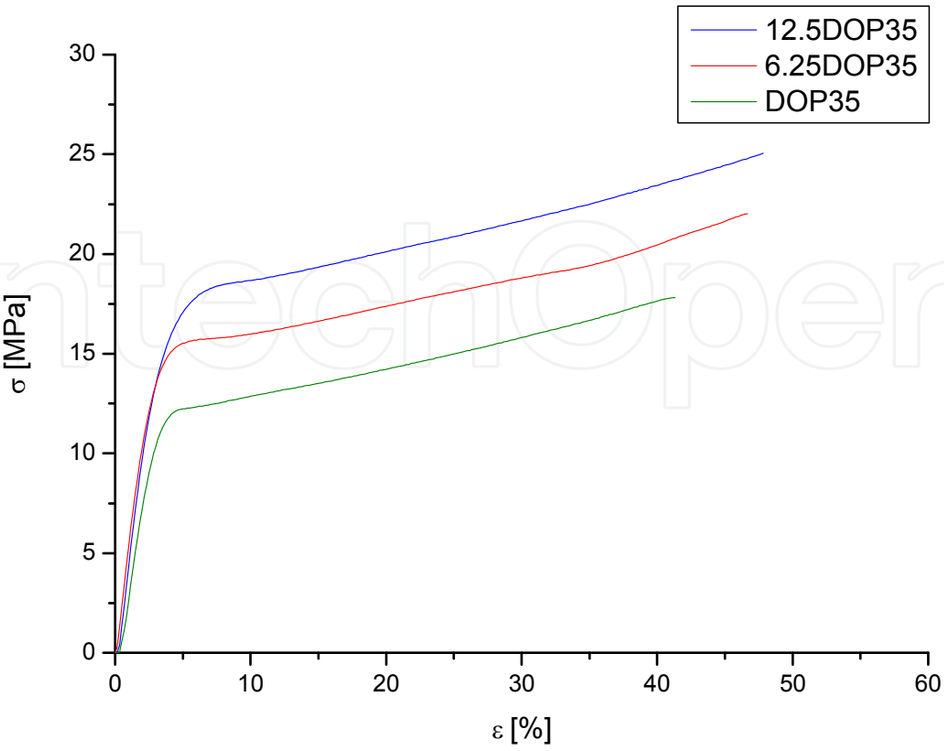


Fig. 18. The tensile stress-strain curves for samples prepared with 35% of DOP.

6. Conclusions

Taking into consideration obtained results we can conclude that type and amount of applied plasticizer as well as incorporation of inorganic phase into CAB matrix affected mechanical properties of the examined samples. Changing the type and concentration of the plasticizer, and amount of inorganic phase can modify the strength and extensibility of the materials. The higher the amount of incorporated silica, the harder and more brittle the material, however exhibiting good flexibility at 30 and 35% plasticizer concentration. All of the plasticizers investigated, excluding TEC, caused an antiplasticization effect at concentration 30% resulting in an increase in tensile strength, in comparison with the values at 25%. At higher concentration of plasticizers (35%) the additives caused plasticization reflected as a decreases in tensile strength and an increase in elongation at break values. Regarding the influence of inorganic phase incorporated into polymer matrix, the tensile strength was substantially improved, as compared with neat CAB, regardless of the plasticizer type.

Among all plasticizers, DEP was found to be the least efficient for CAB, as well as for organic-inorganic hybrids. Low plasticization efficiency showed also TEC. All samples prepared with DEP and TEC showed the noticeable low values of tensile strength as well as poor flexibility, as compared to the same formulations with other plasticizers used in this study. DOP, TBC and TEA were the most efficient plasticizers for CAB and organic-inorganic CAB hybrids. The best formulations in terms of mechanical properties were those containing 30% of above mentioned plasticizers. DOP at 30% concentration was the

most effective to enhance the mechanical properties of CAB and organic-inorganic hybrids, with the highest tensile strength of 31.1 MPa for sample prepared from 87.5/12.5 polymer/TEOS formulation (12.5DOP30). Among citrate plasticizers used in this work, TBC, as well as TEA at 30% concentration were the most effective to improve mechanical properties.

As a final conclusion it can be stated that environmentally friendly citrate plasticizers can substitute phthalates in organic-inorganic CAB hybrids formulations. TBC and TEA can be used as valuable alternatives to DOP, producing materials displaying high values of tensile strength and satisfactory elongation at break.

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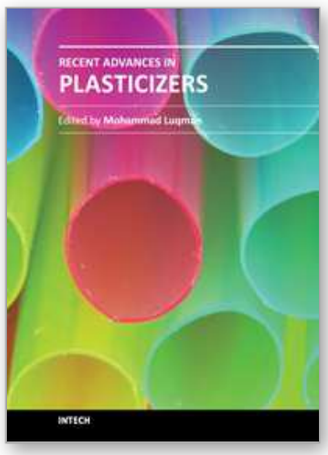

Recent Advances in Plasticizers

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Plasticizers are used to increase the process-ability, flexibility, and durability of the material, and of course to reduce the cost in many cases. This edition covers introduction and applications of various types of plasticizers including those based on non-toxic and highly effective pyrrolidones, and a new source of Collagen based bio-plasticizers that can be obtained from discarded materials from a natural source; Jumbo Squid (Dosidicus gigas). It covers the application of plasticizers in plastic, ion-selective electrode/electrochemical sensor, transdermal drug delivery system, pharmaceutical and environmental sectors. This book can be used as an important reference by graduate students, and researchers, scientists, engineers and industrialists in polymer, electrochemical, pharmaceutical and environmental industries.

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